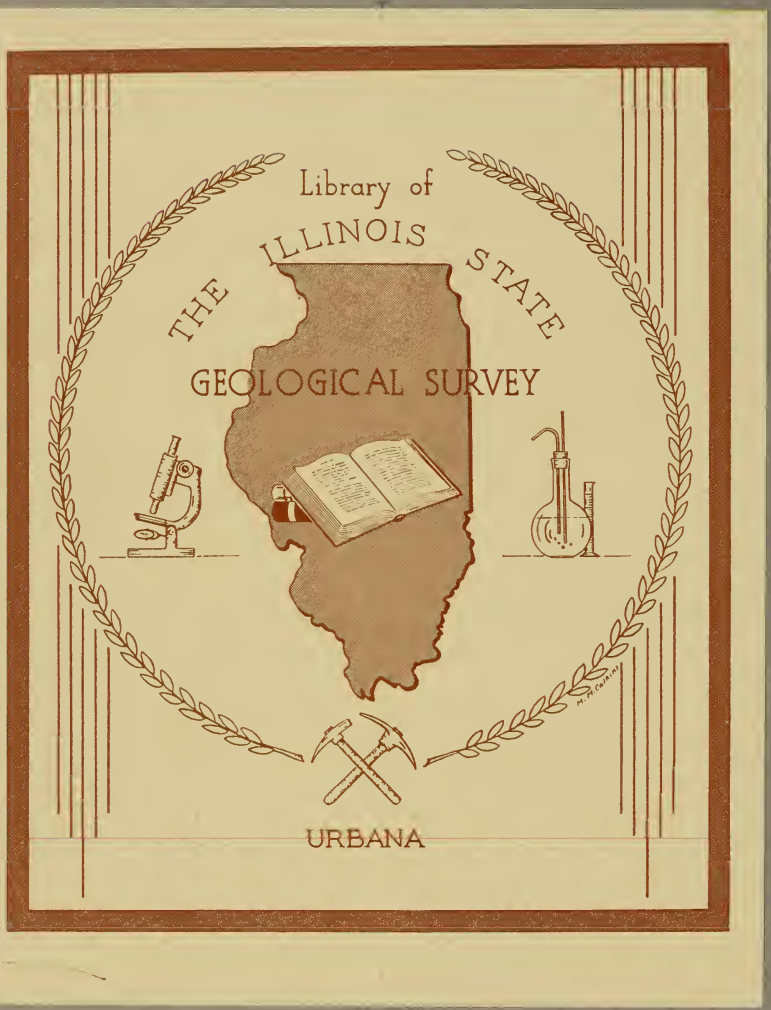

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PROPERTIES OF CLAY

BY

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PROPERTIES OF CLAY[1]

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ABSTRACT

Analyses of many clays by X-ray, optical, chemical and dehydration methods have shown that clays generally are aggregates of extremely minute crystalline particles of one or more species of a small group of minerals known as the clay minerals. There are three important groups of clay minerals: namely, kaolinite, illite, and montmorillonite. The optical, chemical, base-exchange, dehydration, and lattice structural characteristics of the clay minerals are considered.

Replacements within the lattice of the illite and montmorillonite minerals, chiefly Al^{+++} for Si^{++++} and Mg^{++} for Al^{+++}, are considered in relation to base-exchange capacity and particle size characteristics. Physical properties of clays are considered also in relation to the structure of their constituent clay minerals and the character of the exchangeable bases that are present. In general plasticity, bond strength, and shrinkage are relatively high for montmorillonite clays and low for kaolinite clays. In illite clays these properties vary from low to moderately high. Comprehensive information on the influence of specific exchangeable bases and physical properties remains for future researches. Present data are scant and somewhat conflicting.

The distribution of clay minerals in various types of argillaceous sediments is considered. Also the origin of the clay minerals based on synthesis experiments and weathering studies is reviewed.

Clay mineralogy must be considered in making and interpreting mechanical analyses of argillaceous materials, because the clay minerals are affected differently by diagenetic processes and break down on disaggregation with different degrees of ease.

CONSTITUTION OF CLAYS

Analyses of many clays by X-ray, optical, chemical, and dehydration methods have shown that clays generally are aggregates of extremely minute particles of one or more species of a small group of minerals known as the clay minerals (19, 30, 45, 49, 98, 132). Kaolinite cannot correctly be considered as the main constituent of all clays, as many clays contain no kaolinite. The clay minerals are crystalline, except for allophane (134), and most clays are composed entirely of crystalline material (19, 49, 60, 68, 98, 132). In addition to the clay minerals, clays may also contain, usually in minor amounts, such constituents as quartz, limonite, and organic material. The so-called colloid content (14, 19, 62, 68, 83, 98) of a clay is the percentage of the mineral constituents, particularly the clay minerals, that are smaller than a certain size.

Aluminum hydrates are also present in a few clays, and in some clayey substances they are the essential constituents. These materials are not considered in the present paper.

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CLAY MINERALS

In recent years detailed mineralogical analyses have been made of a large number of different clays, and they indicate that there are three (31, 46) important groups of clay minerals: kaolinite, montmorillonite, and illite. Almost all clays are composed of one or more members of these three groups. Other clay minerals occur in few clays, generally in minor amounts.

KAOLINITE GROUP

The chief member of this group is kaolinite which has the composition $(OH)_8Al_4Si_4O_{10}$ (133). Anauxite, similar to kaolinite except for a SiO_2 to Al_2O_3 molecular ratio of about 3 instead of 2, is not a common mineral. Dickite and nacrite, similar in composition to kaolinite but with slightly different crystallographic forms, have been placed in this group. They are occasionally found as very rare constituents of argillaceous sediments. An iron analogue of kaolinite has been suggested by several investigators, but has not been proved definitely.

MONTMORILLONITE GROUP

This group takes its name from the mineral montmorillonite with the composition $(OH)_4Al_4Si_8O_{20} \cdot XH_2O$. Magnesium (46, 135) is practically always present although it is not usually written in the formula (67). Beidellite (90) which has a SiO_2 to Al_2O_3 molecular ratio of 3 and nontronite (59), in which aluminum has been replaced by ferric iron are reputedly members (96, 132) of the montmorillonite group. Saponite (39) in which the aluminum has been replaced by magnesium can be classed as a montmorillonite.

ILLITE GROUP

The third group of clay minerals has been called by various workers, hydromica, mica-like clay mineral (31, 94), sericite-like mineral (47), potash-bearing clay mineral (132). Grim, Bray, and Bradley (51) showed that there is close but not complete similarity of these minerals to muscovite, and that the composition varies within limits which have not yet been circumscribed. They suggested the name illite for this group of clay minerals and recently advanced the general formula (46) $(OH)_4K_\gamma(Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)(Si_{8-\gamma} \cdot Al_\gamma)O_{20}$, in which the value of γ varies from about 1 to 1.5. After future work has determined the range of variations of members of the illite group, it may be desirable to give specific names to members.

MISCELLANEOUS CLAY MINERALS

Halloysite minerals (134).—The exact importance of the halloysite minerals awaits the analysis of additional clays, but work to date suggests that they are not very widely distributed. Mehmel (107) has shown that there are two closely related halloysite minerals: one, $(OH)_{16}Al_4Si_4O_6$, he designates as halloysite, the other $(OH)_8Al_4Si_4O_{10}$, as metahalloysite. The latter forms from the former by the loss of $2H_2O$ on heating to 50°C. Hendricks (64) has suggested the names hydrated halloysite and halloysite, respectively, for these minerals, thus retaining the name halloysite for material of the composition to which it was first applied.

Allophane.—This name has long been used for material that recent work shows to be mostly amorphous. Ross and Kerr (134) suggest that allophane be used to include all non-crystalline mutual solutions of silica, alumina, and water that may contain minor amounts of bases even though the proportion of these constituents may vary. Many mineral names have been proposed for such material.

The term "allophane" or allophaneton (144, 148) has been used widely in Europe, particularly by ceramists, to designate the portion of a clay that is soluble in hydrochloric acid. Allophane (usage of Ross and Kerr) and the montmorillonite minerals are more acid soluble than the other clay minerals, but the use of allophane based on acid solubility has no mineralogical significance (92, 105) chiefly because the effect of variations in particle size is ignored.

Magnesium clay minerals.—Evidence is increasing that certain clay minerals that contain appreciable magnesium or are hydrous magnesium silicates are common constituents of clays. Some of these minerals are definitely members of the montmorillonite group and should be classed as saponite or intermediate members between saponite and montmorillonite. Concerning others the evidence is not clear.

Fersman (38) first suggested the existence of a series of minerals between paramontmorillonite and parasepiolite, which he called palygorskites. Paramontmorillonite and parasepiolite were considered to be acicular forms of montmorillonite and sepiolite. The xylotile group was considered to contain the iron analogues of the palygorskites. De Lapparent (25) has suggested on the basis of thermal analysis that palygorskites are mixtures of kaolinite and sepiolite.

Considerations of possible minerals in a series between hydrous aluminum silicates and sepiolite have encountered important differences in the X-ray diffraction characteristics (23, 155) of sepiolite and montmorillonite. De Lapparent (23, 26) has suggested that in certain of the

clay minerals Mg_3 replaces Al_2, that is, all possible positions are occupied. The name attapulgite was suggested by de Lapparent (23) for minerals of such characters, with examples from Attapulgus, Georgia, and Mormoiron, France. Attapulgite is believed to be flake-like.

Additional research is necessary before the importance, character, and classification of the magnesium clay minerals can be established. Von Englehardt (155), de Lapparent (26), and Serdyuchenko (141) have recently discussed the problems of these clay minerals.

Other clay minerals.—It is not certain that all minerals that should properly be classed as clay minerals have been found. Also there remain old mineral materials for which distinctive names were suggested and which must be investigated in the light of modern analytical procedures to determine whether they are mixtures, duplications of other species, or specific minerals. An example of such material is bravaisite.

PROPERTIES OF CLAY MINERALS

The clay minerals are probably monoclinic in form, though an orthorhombic form has been suggested for some of them (94), and have as their prime characteristic a pronounced basal cleavage. Kaolinite (133) has a hardness of 2.5 and a density of 2.58–2.59. The hardness and density of the other clay minerals have not been determined precisely. Kaolinite and the halloysite minerals are white; the other clay minerals vary from white to yellow or green.

OPTICAL PROPERTIES

The optical properties of the clay minerals insofar as they are known are given in Table I. Clay minerals commonly occur in particles too small for optical study. The individuals can, however, be aggregated together uniformly and fairly precise measurements (14) can be obtained from the aggregates.

Correns and Mehmel (17), and Van Baren (153) have shown that the indices of refraction of some clay minerals vary for different immersion liquids. The variation is greatest for minerals of high base-exchange capacity. Van Baren concluded that liquids that contain the (NH_2) group exerted a particularly strong influence on indices of refraction.

Correns and Mehmel (17) showed that the indices of refraction of some clay minerals vary when they are heated to relatively low temperatures (200°C.). Kaolinite seems to be less affected than the other clay minerals.

TABLE I

OPTICAL PROPERTIES OF CLAY MINERALS

		γ	β	α	$\gamma-\alpha$	$2V$	*Optical Character*	*Dispersion*	*Extinction*	*Orientation of Bisectrices*
Kaolinite group	Kaolinite and Anauxite	1.570–1.560	1.569–1.559	1.563–1.553	.006	24°–50°	(−)	p>V	1°–3½°	$BX_a = X \wedge$ base normal = 1°–3½°
	Nacrite	1.566–1.563	1.563–1.562	1.560–1.557	.006	40°–90°	(+) or (−)	p>V or p<V	10°–12°	$BX_a = X \wedge$ base normal = 10°–12°
	Dickite	1.566	1.563–1.561	1.560	.006	52°–80°	(+)	p<V	15°–20°	$BX_0 = X \wedge$ base normal = 15°–20°
Montmorillonite group	Montmorillonite	1.530–1.500		1.505–1.470	.035–.025	7°–25°	(−)			$BX_a = X$ about ⊥ to base
	Beidellite	1.560–1.530		1.530–1.500	.035–.025	small	(−)			BX_a X about ⊥ to base
	Nontronite	1.610–1.560		1.575–1.530	.035–.030	small	(−)			$BX_a = X$ about ⊥ to base
	Saponite	Indices of refraction similar to montmorillonite								$BX_a = X$ about ⊥ to base
Illite group		1.605–1.565		1.570–1.535	.035–.030	small	(−)			$BX_a = X$ about ⊥ to base
Halloysite group	Halloysite (metahalloysite of Mehmel)	Mean index = 1.561–1.549			very slight					
	Hydrated halloysite (halloysite of Mehmel)	Mean index = 1.542–1.526			very slight					
Allophane		Amorphous n = 1.496–1.470								
Mg-clay minerals		Some of these minerals have indices of refraction similar to those of montmorillonite								

TABLE II

CHEMICAL COMPOSITION OF CLAY MINERALS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
SiO_2	46.90	45.56	54.32	48.60	48.80	47.28	46.06	44.0	53.68	50.10	52.79	44.75	40.22	33.96	25.19	53.7	53.6
Al_2O_3	37.40	37.65	29.96	20.03	21.08	20.27	12.22	3.6	.60	25.12	24.99	36.94	35.41	31.12	36.53	9.0	10.6
Fe_2O_3	.65	1.35	2.00	1.25	.92	8.68	18.54	29.0		5.12	4.68	.31		tr	.78	3.6	6.5
FeO							.28			1.52	1.10					.2	.3
MgO	.27	.07	.14	5.24	4.84	.70	1.62	2.1	25.34	3.93	2.70				.02	9.6	4.6
CaO	.29	.10	.32	1.72	1.36	2.75	1.66		.52	.35	.09	.11	.73	2.26	.04	1.2	2.1
K_2O	.84	.11							.07	6.93	5.86	.60			.10	.5	.5
Na_2O	.44	0.16	.37			.97			3.00	.05	.20		.09			.9	.8
TiO_2	.18	.19					.84			.50							
Ign. loss										6.82	7.14						
Total										100.44	99.55						
H_2O-		.76	.84	21.52	20.92	19.72	17.26	18.7	7.28	1.90	5.56	2.53	23.67	12.84	21.20	9.7	11.6
H_2O+		13.66	11.80						8.24	7.18	6.83	14.89		20.28	15.76	11.6	9.4

1. Kaolin, Zettlitz, Czechoslovakia. *Prof. Paper 165-E, U. S. Geol. Survey*, 1931.
2. Kaolinite, Sand Hill, N. Carolina. *Prof. Paper 165-E, U. S. Geol. Survey*, 1931.
3. Anauxite, Bilin, Czechoslovakia. *Prof. Paper 165-E, U. S. Geol. Survey*, 1931.
4. Montmorillonite, Montmorillon, France. *Jour. Amer. Cer. Soc.*, 9, 1926.
5. Montmorillonite, Ardmore, S. Dakota. *Jour. Amer. Cer. Soc.*, 9, 1926.
6. Beidellite, Beidell, Colorado. *Jour. Amer. Cer. Soc.*, 9, 1926.
7. Iron-rich beidellite, Spokane, Wash. *Jour. Amer. Cer. Soc.*, 9, 1926.
8. Nontronite (probably impure), Nontron, France. *Ann. Ch. Phys.*, 36, 1927.
9. Saponite, Hector, California. *Amer. Min.*, 21, 1936.
10. Illite, Calhoun County, Illinois. *Amer. Min.*, 22, 1937.
11. Illite, Grundy County, Illinois. *Amer. Cer. Soc.*, 22, 1939.
12. Halloysite (meta-halloysite of Mehmel), Liege, Belgium. *Prof. Paper 185-G, U. S. Geol. Survey*, 1934.
13. Hydrated halloysite (halloysite of Mehmel), Colorado. *Jour. Washington Acad. Sci.*, 7, 1917.
14. Allophane, Liege, Belgium. *Prof. Paper 185-G, U. S. Geol. Survey*, 1934.
15. Allophane, Dutchess County, New York. *Prof. Paper 185-G, U. S. Geol. Survey*, 1934.
16. Mg-clay mineral (Attapulgite of de Lapparent), Attapulgus, Georgia. *Compte Rendu*, 200, 1935.
17. Mg-clay mineral (Attapulgite of de Lapparent), Mormoiron, France. *Compte Rendu*, 201, 1935.

CHEMICAL PROPERTIES

Analytical data to show the chemical composition of the clay minerals are given in Table II. The kaolinite and halloysite minerals (133) do not contain alkalies or alkali earths and no definite examples of iron replacing aluminum have been found. In the kaolinite minerals (133) the molecular silica to alumina ratio varies, and there seems also to be a variation in the water content. The composition of members of the illite (51) and montmorillonite (135) groups varies between wide limits because of replacement of aluminum by ferric iron, a variable molecular silica to R_2O_3 ratio, and the presence of variable amounts of alkalies and alkali earths. Allophane (134) may vary within wide limits. Little is known of the precise composition of the magnesium clay minerals (26, 155), but considerable variability will no doubt be found.

The general similarity of the chemical makeup of all clay minerals and the variability of the composition of individuals cause it to be difficult or impossible to interpret the mineral composition of a clay from its chemical composition alone.

BASE-EXCHANGE CAPACITY

Base-exchange capacity (35, 46, 69) values for the important groups of clay minerals are given in Table III. The halloysite minerals seem to have a low capacity although Edelman (28) has some data which do not concur entirely. The capacity of the allophane minerals is not known. Precise information is not available for the magnesium clay minerals, but for some of them, at least, the capacity is fairly high.

TABLE III

BASE EXCHANGE CAPACITY IN MILLIEQUIVALENTS PER 100 GRAMS

Montmorillonite	60–100
Illite	20– 40
Kaolinite	3– 15

Exchange capacity is known to vary with particle size. Kelley (81) has recently shown very great increases of base-exchange capacity with extreme dry grinding of aluminum silicate minerals. Other aspects of base-exchange are discussed in other papers in this volume.

DEHYDRATION PROPERTIES

Curves showing the relation of water loss to temperature for the clay minerals on which such data are available are given in Figure 1. Several French investigators (123, 150) have seized on differences in the de-

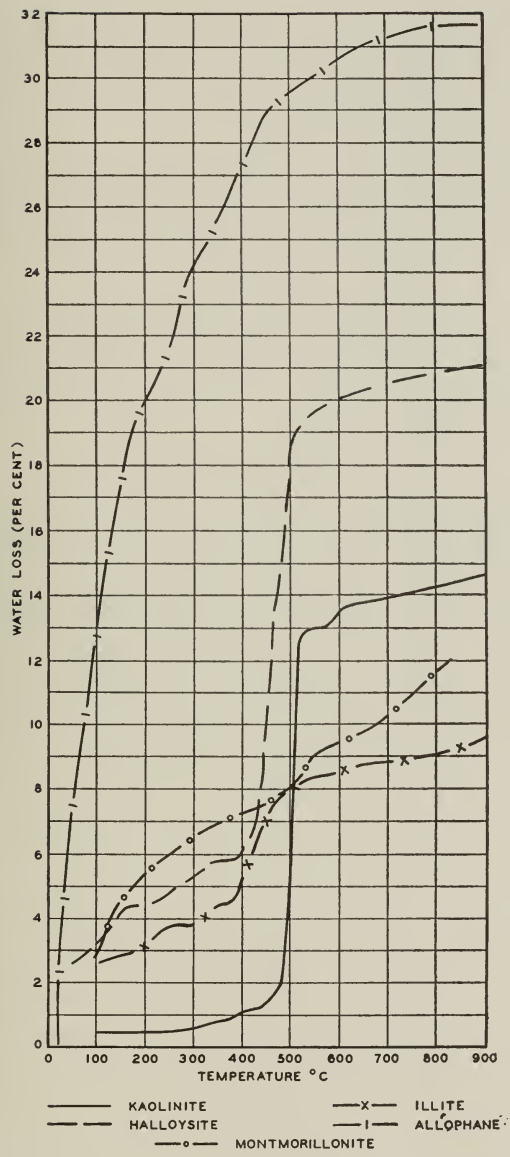

FIG. 1.—Dehydration curves of clay minerals. Kaolinite data from Ross and Kerr (133); halloysite and allophane data from Ross and Kerr (134); illite data from Grim, Bray and Bradley (51); montmorillonite data from Nutting, *Circular 3, U. S. Geol. Survey*, 1933.

hydration properties of the clay minerals as means of mineralogical analyses. Recent work by Kelley (83), indicating that there is appreciable variation in dehydration properties depending on particle size, means that dehydration characteristics must be used with considerable caution in the mineralogical analyses of clays.

Recent researches (11) of the hydration characteristics of montmorillonite at low temperatures have indicated that water is lost in units providing a step-like curve. Recent work also indicates that the hydration characteristics in this temperature range vary with the character of the exchangeable cation (69).

Montmorillonite is reported as rehydrating (67) after heating to 550°C., kaolinite after heating to 500°C. Few precise data are available on this point although the property is important in determining certain commercial utilizations of clays.

LATTICE STRUCTURE

Following generalizations of Pauling (124) in 1930, work in several laboratories has well established the general structural characteristics of the clay minerals (9, 51, 57, 63, 67, 68, 69, 94, 96, 107). Two structural units are involved. One unit is the alumina or aluminum hydroxide unit, which consists of two sheets of close-packed oxygens or hydroxyls between which aluminum atoms are embedded in such position that they are equidistant from 6 oxygens or hydroxyls. Actually only two-thirds of the possible aluminum positions are occupied in this structure, which is the gibbsite structure. The mineral brucite possesses a similar structure except all the possible aluminum positions are occupied by magnesium. The second unit consists of a sheet of silica tetrahedral (SiO_4) groups linked to form a hexagonal network of the composition Si_4O_{10} when repeated indefinitely. This unit may be viewed as a sheet of loosely packed oxygen atoms with each oxygen linked to two silicon atoms directly beneath. The silicon atoms are in tetrahedral positions, three valencies being satisfied by linkage to three oxygens in the overlying sheet. The fourth silicon valency is satisfied below by an oxygen atom such that silicon valency is analogous to the common (OH) group of gibbsite.

Montmorillonite (67) consists of structural units of one gibbsite sheet between two sheets of silica tetrahedral groups (Fig. 2). The structural units are stacked one above another in the direction of the c-axis, and they are loosely held together with water present between the units. The c dimension varies with the H_2O content, and the mineral is said to have an expanding lattice.

The magnesium contained by montmorillonite probably, at least in part, exists as replacements by Mg^{++} of Al^{+++} positions in the gibbsite layer thereby providing an excess charge on the lattice. The origin of this excess charge is in the center of a unit about 9Å thick. At the surface of the unit the charge can be assumed to have the strength necessary to hold exchangeable bases. The charge is not strong enough to hold together tightly the units making up montmorillonite as water may enter between them causing the lattice to expand. It may be considered that

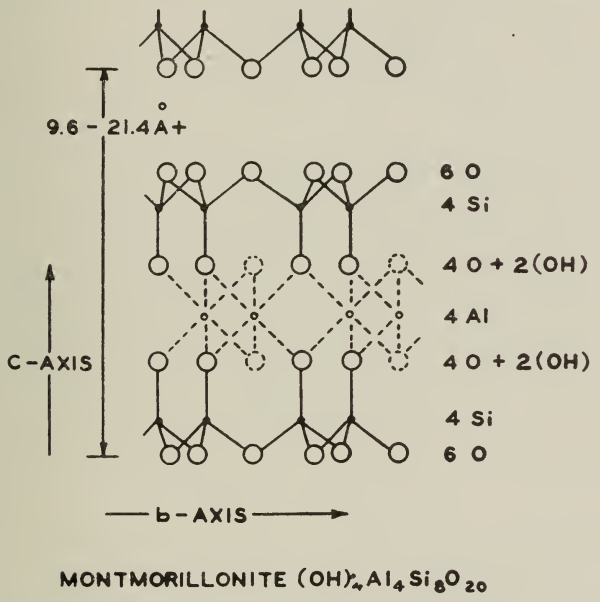

FIG. 2.—Schematic presentation of crystal structure of montmorillonite.

the hydration of the exchangeable cation causes the units to be pushed apart. Hence, assuming replacements of the Al^{+++} gibbsite positions, montmorillonite is built up of units loosely held together as a consequence of which it can expand, or very readily cleave, *e.g.*, on agitation in water, into extremely thin flakes giving a huge surface area to a mass of the mineral. Also on this assumption the flakes would carry a charge on their surfaces adequate to hold exchangeable bases. The high exchange capacity and ability to break down into extremely minute size, which are characteristics of montmorillonite, may be accounted for in this way. Replacement of slightly less than 20 per cent of the Al^{+++} gibbsite positions with Mg^{++} would provide a base-exchange capacity of about 100

milliequivalents per 100 grams. Some of the Al^{+++} may be replaced by Fe^{+++}, with the result that the lattice charge would be unaffected.

Another type of replacement may occur in the montmorillonite structure; that is, Si^{++++} by Al^{+++} in the silica tetrahedral sheets. This replacement provides an excess charge originating near the surface of the 9Å units, and, therefore, stronger than the charge resulting from the other replacements. Such charges are assumed to be adequate to hold the units in position so that water cannot enter and cause expansion. In the

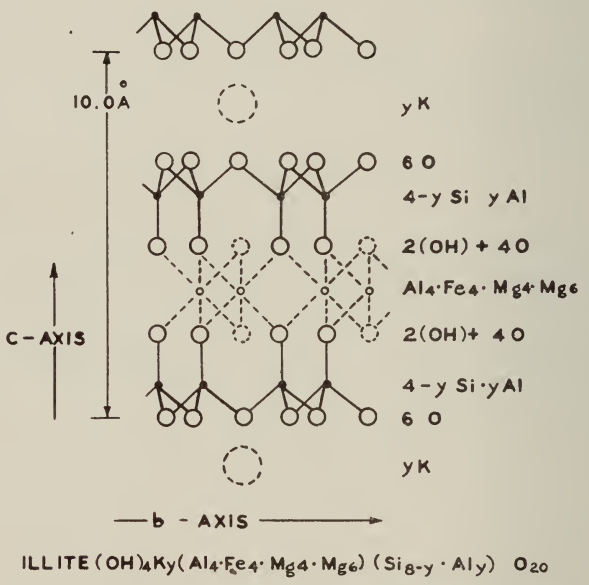

FIG. 3.—Schematic presentation of crystal structure of illite.

montmorillonite minerals, this type of replacement is limited to an amount insufficient to prevent expansion. In illite the replacement exists to the extent that about 15 per cent of the Si^{++++} positions are occupied by Al^{+++}. The excess charge resulting from this replacement in illite is satisfied by potassium ions and the units are held together without the power of expanding. It may be considered that the units are held together through the potassium ions. Figure 3 shows that the illite and montmorillonite structures are similar except for the replacement in the tetrahedral layer with the resulting potassium ions and the absence of expanding power. The potassium ions of illite are replaceable when they occur on an accessible surface. In the illite structure there are also replace-

ments in the gibbsite sheet, some of which may provide an excess charge available for a replaceable base. In illite, however, the unit layers do not expand and make available a huge surface area between the units for base exchange. As a consequence, exchange capacity is lower for illite than for montmorillonite. Also because the unit layers are held together tightly, illite does not tend to break down by agitation in water into as small or as thin flakes as montmorillonite.

Both illite and montmorillonite may carry some Mg^{++} in possible Al^{+++} positions not occupied in gibbsite, *i.e.*, in brucite positions.

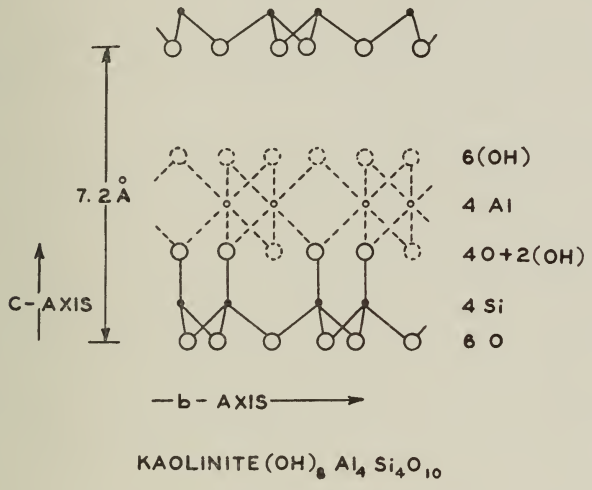

FIG. 4.—Schematic presentation of crystal structure of kaolinite.

The kaolinite (56, 57, 63) structure is composed of a gibbsite sheet with a single sheet of silica tetrahedral groups (Fig. 4). The lattice structure does not expand with varying water content, and no replacements by iron or magnesium of the aluminum in the gibbsite lattice have been proven. To account for variations in the silica to alumina ratio of members of this group of clay minerals, it was first suggested (57) that Si^{++++} replace Al^{+++}. A recent more favored explanation (63) is that some of the Al^{+++} positions are vacant with corollary changes of O and OH to balance the charges in the lattice. Base-exchange capacity must be attributed to broken bonds on the edges of fragments and hence is small. The kaolinite structure (Fig. 4) is not of the expanding type, probably because of the attraction between O and OH layers, which are adjacent when kaolinite units are stacked one above the other, in contrast with

montmorillonite in which the *O* layers are adjacent. Consequently the mineral does not readily break down into flakes of extremely small size.

RELATION OF PHYSICAL PROPERTIES OF CLAY TO MINERAL COMPOSITION

CONCEPT OF STRUCTURE OF CLAY

As the clay minerals occur in flake-shaped particles, it follows that most clays are essentially aggregates of very minute flakes or plates. The flakes possess forces of varying intensity, which tend to attract individuals to one another and hold them together. The force may be thought of as acting mainly from the flat surface of the flake, because such surfaces make up a very large percentage of the total surface area of the particle. To substitutions within the lattice may be assigned the primary cause of the attractive force.

On the addition of water to clay a film of H_2O develops on the surface of the flakes, probably because of the attractive force and because of the presence of adsorbed cations, which tend to hydrate. The water film, which has been described as having high viscosity, may be considered to have several functions (146). It separates individual flakes, thus causing the force holding the flakes together to act through greater distances and thereby become weaker. It acts as a lubricant between the flakes (146). The water dipoles between the flakes are probably oriented with movement possible along planes of dipole ends. It has been suggested (102) that the flakes are held together more efficiently through oriented dipoles, than through non-oriented molecules, and that the lubricating effect is only possible in the presence of oriented dipoles.

On the surface of the flakes of some clay minerals, there are positions where exchangeable cations can be held. Different cations possess different hydration properties (34, 35, 157); for example, the hydration of the sodium ion is much greater than that of the calcium ion, which in turn is greater than that of the hydrogen ion. It may be considered that the character of the cation, because of its hydration properties, will influence the thickness of the water film around the clay mineral flake. A further controlling factor in the thickness of the water envelope is the distance from the surface of the flake at which the cations tend to be held, which in turn is related to the size and valence of the ion (29). It follows from the foregoing discussion that sodium montmorillonites would possess a tendency to build up a thicker water film than would hydrogen montmorillonites. This is in agreement with the well known fact that sodium

bentonites, which are composed of montmorillonite, swell markedly in water, whereas hydrogen bentonites swell little or not at all.

The physical properties of clay, *i.e.*, plasticity, bonding strength, shrinkage, retention of form, *etc.*, may be ascribed (1) to the structure and composition of the clay mineral, which determine the particle size on working with water and the attractive force between particles, and (2) to the character of the exchangeable base. By composition is meant the makeup of the clay mineral, particularly in regard to substitutions within the lattice. Two montmorillonites identical except for differences in Mg^{++} replacements of Al^{+++} gibbsite positions may be expected to impart different physical properties to clays containing them. In other words the properties depend not only on the presence of montmorillonite, but on the composition of the particular montmorillonite. The water film on the surface of the clay mineral flake results from both the structure-composition factor and the factor of exchangeable base. The phenomenon of plasticity results from the interplay of the attractive force tending to draw the clay mineral flakes together, the thickness of water film keeping the flakes apart, and the lubricating properties of the water film. A clay composed of flakes with high attractive force, and thin water film because of an exchangeable cation held close to the flake surface of low dehydration ability would on the basis of this concept yield a sticky plastic mass. A clay composed of flakes with high attractive force and thick water film because of a highly hydrated cation that is held a greater distance from the flake surface, or a clay composed of clay mineral with low attractive force, would yield a plastic mass with less stickiness.

Although the present objective is not to consider the influence of constituents other than the clay minerals on the properties of clays, owing to the fact that much information on this subject has been published, it may be pointed out that angular grains of quartz, feldspar, *etc.*, would disrupt the makeup of a clay leading to plasticity, just as grit, between two lubricated steel surfaces, disrupts the action of a lubricant. The well known tendency of such material to reduce plasticity is in accord with the above concept. It is well known that colloidal organic material influences the properties of clays. The exact mechanism of the effect is not clear, but in general the action results from an effect on the film of water. The influence of organic constituents is an important and promising field for needed research.

Data at hand permit only the consideration of the influence of montmorillonite, illite, and kaolinite on the properties of clays.

INFLUENCE OF THE MONTMORILLONITE MINERALS

It follows from the foregoing discussions that a clay composed of montmorillonite on being worked with water consists of a very large number of extremely minute flakes that have charges on the surface of the flakes adequate to hold exchangeable bases, and provide a certain attractive force between particles. Conditions are proper, therefore, for the development of the water film on the flakes, and with the attractive force between flakes, the situation fulfills the requirements for the plastic state in clays. The great number of such flakes in a montmorillonite clay, or more properly the great number of water films between flakes along which slippage can take place, indicates that the order of plasticity of such clays will be high. Also, the huge surface area for the development of water films indicates that water of plasticity and drying-shrinkage will be relatively high. The great surface area that possesses attractive force suggests that the bonding power will also be high. Although the attractive force, because it comes from the center of the cell, is not great individually, the huge total number of such charges dictates that their mass effect will be large.

Montmorillonite clays have high base-exchange capacity, and since the character of the exchangeable cation is closely related to the development of the water film covering the flakes, the unfired properties of montmorillonite clays will exhibit considerable variation, depending on the exchangeable cation present.

INFLUENCE OF THE ILLITE MINERALS

Clays composed of illite are aggregates of flakes that have attractive forces on their surfaces. Like clays composed of montmorillonite, conditions are proper for the development of water films surrounding the flakes and for the existence of the plastic state when the clay is worked with water. However, as flakes of illite are larger than those of montmorillonite, fewer are present in a given volume of clay. The total surface area in an illite clay would therefore be smaller and fewer water films between flakes along which slippage would be present. The plasticity of illite clays would therefore be relatively less than that of montmorillonite clays. It follows that the water of plasticity, drying shrinkage, and the influence of exchangeable bases on surface properties would be lower in illite than in montmorillonite clays. A similar line of reasoning shows that bonding power would also be less for the illite clays.

Some illite clays have properties approaching those of bentonites, whereas others have much less plasticity, bond strength, *etc.* This varia-

tion has been attributed (48) to variations in the amount of replacement of Si^{++++} positions by Al^{+++} in the silica tetrahedral sheets of the lattice. When such replacements are few the mineral approaches montmorillonite; when they are large the structure is similar to that of muscovite. Variations in properties would be anticipated with the amount of such replacement.

INFLUENCE OF THE KAOLINITE MINERALS

The kaolinite cell does not undergo replacements tending to develop excess charges on the lattice, and the mineral has low base-exchange capacity. The units of kaolinite are held together securely enough along the *c*-axis so that in the presence of water the mineral does not tend to break down into extremely small and extremely thin flakes.

Clay composed of kaolinite may be viewed as an aggregate of uncharged small flakes that are not as small as those of montmorillonite or some illite clays. There is, therefore, slight tendency to form water films on the flakes and for the individual flakes to attract each other. Consequently bond strength, drying shrinkage, and general plastic properties should be low. Water of plasticity should be well below that of montmorillonite clays and subject to variation depending on the size of the kaolinite particles. Properties of the kaolinite clays depend little on the character of the exchangeable base.

Theoretically it would seem that montmorillonite and some types of illite clays should have very much greater plastic properties and bonding strength than kaolinite clays and other types of illite clays. This is in agreement with the well known fact (32) that a small amount of montmorillonite clay, for example, bentonite, added to clays of low plasticity and bond strength greatly increases these properties. For these reasons and also because of petrographic analytical data for a wide variety of clays (14, 49, 50), the writer has reached the conclusion that the unfired properties of clays are frequently determined to a large degree by the amount of montmorillonite-type clay mineral or illite of a certain type that is present. For example, in china clays, which are kaolinite clays, very small amounts of montmorillonite or illite may be the chief factor in determining properties—the influence being out of all proportion to the abundance of these minerals. In fact the quantity may be too small to permit detection when a bulk sample is studied. Only by fractionation (14) of the finest grade sizes does the constituent that may be largely responsible for the properties become evident.

RELATION OF PHYSICAL PROPERTIES TO EXCHANGEABLE BASES

Only a very incomplete discussion of this subject is possible because of a general unsatisfactory condition of the available data, which are scant and in part contradictory. There are many reports of the influence of electrolytes on clays but they are of little value because the amount of actual base-exchange is not recorded and the data cannot be interpreted. The lack of adequate tests for measuring such properties as plasticity is an added difficulty.

Primarily the influences of various cations (34, 35, 46) on many physical properties rests with the degree of their hydration and the distance they tend to be held from the surface of the particle, and consequently with the water film developed, its character, and the distance the clay mineral flakes are kept apart. By characteristics is meant, for example, the possible perfection of orientation of the water dipoles—there is some reason to believe that the degree of orientation may vary with the cations present. Sodium ions carry much water and are loosely tied to the surface of the flake. Calcium and magnesium ions are more solidly held and carry less water, and hydrogen, aluminum, and iron are firmly held and carry less water than the bivalent ions. A further influence, vital to the understanding of some properties, is the disrupting influence of some cations, particularly Na^+, in clays of certain types. Highly hydrating Na^+ in montmorillonite tends to produce a spreading apart of the structural units along the *c*-axis with a consequent break-up of the clay particle into extremely minute flakes. There is much less tendency for spreading of the structural units of a H^+ montmorillonite clay so that on working with water, a Na^+ montmorillonite clay will be made up of a greater number of smaller flakes than an H^+ montmorillonite clay. The character of the exchangeable cation, therefore, also influences properties because of its influence on the particle size distribution of the clay when worked with water.

Some investigators (145) consider that Na^+ increases the plasticity of clays, others (30, 35) that this property is decreased. Cations of low hydration, such as H^+ and the trivalent ions Al^{+++} and Fe^{+++}, impart low plasticity to clays (30, 35, 145). Recent studies (30, 35) indicate that the best plastic properties are found when an ion of intermediate or relatively low hydration, like Ca^{++}, is the exchangeable base present. Available data indicate that water of plasticity may be unexpectedly higher for the hydrogen clays than for those carrying alkalies.

Substitution of sodium for other exchangeable bases tends to increase

drying shrinkage (30). Clays with Al^{+++}, Fe^{+++} have lower shrinkage than those carrying Ca^{++} and Mg^{++}, and these clays in turn have less drying shrinkage than those with the Na^{+} ion.

Green strength tends to be higher for H^{+} clays than for clays carrying Na^{+}. Clays with the divalent ions possess an intermediate strength. In some utilizations of clays it is necessary to determine a green and a dry strength of clay in clay-sand mixtures. It is known that H^{+} bentonites have higher green strength than Na^{+} bentonites and that frequently Na^{+} bentonites have greater dry strength than H^{+} bentonites. The explanation for this situation is by no means clear, but it would seem to be related to the differences in the disrupting ability of Na^{+} and H^{+}. That is to say, dry strength is closely related to particle size whereas green strength is more closely related to the thickness and development of the water film on the flakes.

It is well known that almost all clays with high ability for removing the color from oil are composed of members of the montmorillonite group or certain types of illite, and that the efficiency of many of them is increased by acid treatment. It has been suggested (66) that decolorizing ability is related to the presence of H^{+} and Al^{+++} in proper proportions as exchangeable cations.

DISTRIBUTION OF CLAY MINERALS

Work on the mineralogical analysis of argillaceous materials has not been extensive enough to permit a thorough consideration of this subject. Data are particularly scarce for recent sediments, as workers in studying such material usually list only a clay grade and fail to determine its mineral make up. Soil investigators and others are rapidly adding to our understanding of the source and origin of clay minerals, and there is a growing body of information on ancient sediments, but until more is known of recent sediments the complete history of argillaceous materials cannot be well understood. The work of Correns (16–20), considered elsewhere in these reports, on sediments of the South Atlantic illustrates the type of study needed.

Kaolinite is the constituent of residual and sedimentary kaolins, commonly in a relatively pure state. It also occurs in many sedimentary clays, such as the Pennsylvanian underclays and the Cretaceous and Tertiary clays of the Coastal Plains of the Atlantic Ocean and the Gulf of Mexico, commonly mixed with other clay minerals. Numerous analyses showing kaolinite in similar European clays have been recorded (19, 30, 31). Kaolinite has been found in some ancient residual materials, and from the clay fraction of soils formed in warm humid regions.

Nacrite and dickite occur mostly where there has been hydrothermal alteration, and are very rare in sediments. Kaolinite may also have such a mode of occurrence, but as Ross and Kerr (133) have suggested, much of the so-called kaolinite of hydrothermal origin is probably nacrite or dickite.

Anauxite is not a common clay mineral, and is best known from the Ione sediments of California (1). The original occurrence at Bilin, Czechoslovakia, is a weathering product of augite (142).

Minerals of the montmorillonite group are the constituents of bentonites (135). They also compose some sedimentary clays (45) that are not bentonites, and there is some evidence that they are almost always present in the finest grade size of clays, although usually in very minor amounts. Correns (16) has recorded montmorillonite in recent marine sediments. The minerals occur also as residual weathering products and are well known in the soils (12) formed in the north-central part of the United States.

Illite is the constituent of most shales. It is also a very common constituent of sedimentary clays and commonly is mixed with other clay minerals. The clays of the Coastal Plains of the Gulf of Mexico are mostly mixtures of kaolinite and illite. Illite is one of the main constituents of the glacial materials of the United States. The mineral appears to be easily altered and is not apt to be a constituent of residual deposits.

The halloysite minerals have been reported by Correns (16) in sediments of the Atlantic, and by several workers as rare constituents in a variety of sediments associated with kaolinite. A well known American occurrence is in the so-called indianaite, in Lawrence County, Indiana. It has also been recorded from the clay fraction of some soils of the southern United States (62, 84).

The mode of occurrence of allophane is not well known, but it is usually associated with halloysite, according to Ross and Kerr (134).

No data are available on the occurrence of the magnesium clay minerals for the reason that the minerals themselves await precise study and classification.

ORIGIN OF CLAY MINERALS

Data on this subject are still scant, but they are accumulating from synthesis experiments, observations of clay minerals as alteration products in soils and other materials, and chemical studies of hydrous aluminum silicates.

In the field of synthesis experiments the contributions of Noll (112,

113, 114) are particularly significant. His results may be summarized as follows: In the system Al_2O_3-SiO_2-H_2O, pyrophyllite is formed above 400°C., and kaolinite below 400°C. Böhmite results from an excess of Al_2O_3, and amorphous silica from an excess of SiO_2.

In the system Al_2O_3-SiO_2-H_2O that possesses hydroxides of alkalies or alkali earths and has an Al_2O_3:SiO_2 ratio of 1:4, kaolinite forms at 300°C. when the M_2O or MO:Al_2O_3 ratio is less than 0.2:1. When the ratios are higher montmorillonite forms except that increased amounts of potash lead to the formation of first sericite, then potash feldspar. Sericite forms when K_2O:Al_2O_3:SiO_2 = 0.37:1:2. Increasing amounts of MgO favor the formation of montmorillonite. Carbonate and neutral salts of alkalies or alkali earths act like the hydroxides. $MgSO_4$ leads to the formation of montmorillonite, whereas the sulphates of Ca, K, and Na do not.

In the system Al_2O_3-SiO_2-H_2O-K_2O at 300°C. with equal cation concentration, montmorillonite is formed in an alkaline solution, kaolinite in an acid solution. With increased concentration of K_2O, sericite is formed in the alkaline environment, kaolinite in the acid. Above 400°C. pyrophyllite is formed instead of kaolinite.

Ewell and Insley (36) have synthesized kaolinite and beidellite under conditions that seem to agree with those found by Noll. Early synthesis work is difficult to evaluate because prior to the development of X-ray analytical procedure, there was no adequate means of identifying the very fine material produced.

A large literature exists concerning the origin of kaolinite, which has been reviewed by Rösler (131), Harrassowitz (61), and Ross and Kerr (133). Hydrothermal versus supergene origin and the character of acid agent required by a supergene process have been much discussed. Ross and Kerr (133) showed that the material for which there is strong evidence of a hydrothermal origin is generally nacrite or dickite. Recent work (119, 40) has shown that kaolinite is produced from feldspar by the attack of a variety of acids including organic acid in soils.

Schwarz (140) and his colleagues have concluded that in the change of feldspar to kaolinite there is first a hydrolysis of the original material into silica and alumina sols followed by a recombination into kaolinite, whereas Dittler (27) believes there is a stochiometrical reaction. This point has been reviewed in detail by Harrassowitz (61).

Soil studies have shown that under some conditions of soil formation kaolinite or halloysite is formed, under others the montmorillonite minerals are produced. Soil investigators (8) have shown that the parent

material is relatively unimportant if the soil forming process is long continued, and that climate and land form are the important factors. Rainfall, temperature, drainage, plant cover, *etc.*, perhaps as they determine the pH of the soil water, are believed to determine the character of the soil material. Much work (20, 73, 74, 130) has been done on the relation of the chemical composition of soils and the abundance of clay material to climatic factors. Unfortunately these chemical data cannot safely be interpreted mineralogically and information on the relation of soil-forming conditions to the origin of clay minerals is only beginning to appear.

Bray (12) has shown that minerals of the montmorillonite group are forming in Illinois soils. Von Englehardt (156) and also Correns and Schlünz (18) have pointed out that constituents of several German soils belong to the same group. Several soils from the southern part of the United States have been investigated by Bray and the writer in unpublished studies and they contain halloysite or kaolinite. Hendricks and Fry (62), and Kelley, Dore, and Brown (84) identified kaolinite or halloysite, and montmorillonite minerals in various soils, and found the same clay mineral constituent in soils from widely scattered locations.

Tomlinson and Meier (147), and Noll (116) reported the formation of montmorillonite as an alteration product of the constituents of basic igneous rocks under conditions that suggested to them that the montmorillonite was formed because of the presence of magnesium.

On the basis of chemical laboratory research, Mattson (103, 104) has suggested that soil colloids possess a tendency to alter their composition so that their isoelectric point coincides with the prevailing pH of the soil water. Since the isoelectric pH decreases with an increase in the silica content, it might be expected that at say pH 4.5 colloidal material reasonably high in silica would form and at say pH 7.5 laterization would take place. Mattson has indicated that this is in agreement with the tendency of laterites and kaolinites to occur in the warm regions, and with the available data on the chemical composition of soil colloids. There is a suggestion that less siliceous material, that is, hydroxides, kaolinite and halloysite tend to form under warm climatic conditions, and more siliceous material, that is, the montmorillonite minerals tend to form under cooler conditions.

The conclusions of Mattson do not seem to agree with the conclusions of Noll based on his synthesis work. It is clear that additional work is needed before satisfactory generalizations on the relation of clay minerals to their conditions of formation can be developed.

The origin of allophane is not known except that it is commonly associated with halloysite. The conditions whereby halloysite is formed rather than kaolinite have not yet been ascertained. Likewise the factors determining the origin of the magnesium minerals are not known.

Illite minerals appear to form at times from feldspar as an intermediate product in the eventual formation of kaolinite under conditions that have not been clearly described. Illite is altered by weathering processes and is not itself apt to be a result of such processes. Probably the prime mode of origin of illite is in diagenetic processes, as will be considered later.

CLAY MINERALOGY IN RELATION TO MECHANICAL ANALYSES

Early mechanical analyses grouped clay into one size-grade, and silt as another without any attempt to subdivide the silt and clay grades. At present the tendency is to segregate the finest fractions into many size grades. The objectives of such analyses are to determine the size-grade distribution of the natural sediment as a basis for an understanding of its origin or properties and to permit a more adequate study of the mineral constituents. Clay mineral studies indicate that certain characteristics of these minerals must be taken into account in making mechanical analyses.

Cleavage as mentioned above takes place with relative ease between the structural units making up the clay minerals, that is in the plane of the basal surface. Mechanical analyses of argillaceous materials are preceded by a process of dispersion to place the clay in suspension in water. Such a process will tend to reduce the size of the clay mineral flakes in the natural clay by cleaving them and breaking the thin cleavage flakes. For example, thin section study of a bentonite from Louisiana showed it to be composed of montmorillonite in particles that ranged up to 100 microns in diameter. This clay is easily dispersed by simple agitation in water so that all of it shows a particle size of 1 or less than 0.1 micron. Clearly in making mechanical analyses of clays, the measurements made represent the degree of disaggregation and frequently nothing else. The size distribution as determined may have no relation to that of the natural clay. Analyses to be comparable must be made with the same preliminary treatment including the use of the same electrolyte. Analyses of clays composed of montmorillonite and of some illite minerals vary more with the character of the electrolyte used than those composed of other clay minerals, because of their relatively high base exchange capacity.

Lattice characteristics suggest that the montmorillonite minerals should break down more readily than the kaolinite minerals, and that some illite minerals should break down easily. Study of a large number of clays has shown that the montmorillonite minerals and some illite minerals readily break down in a suspension into particles of less than 0.1 micron in diameter. Kaolinite and most illite minerals are broken down with difficulty or not at all to particles of 1 to 0.1 micron in diameter. These characteristics have been used (14) as an aid in studying the mineral composition of clay composed of mixtures of clay minerals.

It may be concluded that mechanical analyses of kaolinite and some illite clays give a fair picture of the composition of the natural clay. Similar analyses of montmorillonite and other illite clays measure little more than the degree of disaggregation.

The possibility of post-depositional mineralogic changes in argillaceous materials is discussed elsewhere, but the probability of such changes and their effect on particle size must be considered if mechanical analyses are considered to have genetic significance.

CONSTITUTION OF THE CLAY GRADE OF NON-ARGILLACEOUS SEDIMENTS

In view of modern clay mineralogy it is no longer adequate to designate the finest portion of sedimentary rocks merely as clay. Descriptions should include data regarding the kind and amount of clay minerals present.

Analyses of sands generally disregard the composition of the finest fractions. Descriptions of insoluble residues of limestone should include identification of the constituents of the clay grades as well as of the coarser grades.

Investigations of the clay minerals in Illinois limestones and dolomites have shown (52) the presence of illite, kaolinite, and montmorillonite-type material. Data on the clay minerals in these limestones and dolomites proved to be of significance in correlation, in working out geologic history, and in certain phases of their economic utilization.

Correns (20) has recently shown the presence of kaolinite, halloysite and montmorillonite in the non-calcareous portion of deep-sea sediments and has derived therefrom important conclusions on the distribution of clay minerals and on the relation of various kinds of deep-sea sediments to each other.

POST-DEPOSITIONAL MINERALOGIC CHANGES IN ARGILLACEOUS SEDIMENTS

It is proposed to consider changes which may be associated with diagenesis and not those associated with more intense metamorphism. Unfortunately there are few direct data available—chemical studies of sorption process cannot safely be interpreted mineralogically, and mineralogical analyses of recent clays are very scant. There is great need for careful study of recently accumulated argillaceous material in order that this subject may be understood, and, therefore, that the complete history of ancient argillaceous materials may be worked out.

There are, however, certain considerations, largely theoretical, which permit a first attempt at the problem. The structure of the montmorillonite and illite minerals are very similar (46). It is easily conceivable that a mud composed of montmorillonite in the presence of available potash would take up the alkali and be changed to illite. Montmorillonite has high adsorptive ability and the structural change would be small. Possibly in fresh water such a change would not take place whereas it would in salt waters. Noll's (113) synthesis work suggests that the pH of the environment and the character of the alkali or alkali earth present would be controlling factors.

Montmorillonite minerals are rarely dominant constituents of ancient sediments, except bentonites, and they have had a peculiar mode of origin, whereas the minerals of this group are present widely in soils. On the other hand illite is a prime constituent of many argillaceous sediments, and it is being altered generally in present weathering processes. This may be taken to suggest that the montmorillonite to illite change is a frequent one in diagenesis processes. The writer (47) has suggested that the illite in the Pennsylvanian shales of Illinois formed after deposition. Evidence has been presented to show that mica may develop in soils heavily treated with potash fertilizer (152).

The same line of reasoning would lead to the conclusion that kaolinite tends to remain unchanged through diagenesis processes. It has little tendency to adsorb alkalies, and its structure is notably different from those of montmorillonite and illite. On the basis of Noll's (113) work, it is possible that kaolinite may under some conditions form from montmorillonite, or under other conditions be altered to another clay mineral. It seems probable, however, that kaolinite usually passes through the diagenesis of the sediment unchanged. Many ancient kaolinite sediments are known—many of the Pennsylvanian underclays are an example.

The halloysite minerals possess some similarities to the kaolinite minerals, and it is possible that accumulations of halloysite may be changed to kaolinite. Possible changes of the magnesium clay minerals are not known. Amorphous allophane could conceivably be changed into most any other clay mineral depending on the character of the environment.

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